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## THERMODYNAMIC PROPERTIES OF NEON

by

[R. D. McCarty and R. B. Stewart]

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② Cryogenic Engineering Laboratory  
National Bureau of Standards,  
Boulder, Colorado

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Abstract

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Analytical functions for calculating values of pressure, volume, temperature, internal energy, enthalpy and entropy of neon are presented for temperatures from 25° to 300°K with pressures to 200 atm. The thermodynamic properties have been calculated by means of an equation of state fitted to selected experimental and theoretically derived P-V-T data; the results are illustrated on a temperature-entropy diagram. The accuracy with which the equation of state represents the P-V-T data in the ranges of temperature and pressure where experimental measurements have been reported is comparable to the accuracy of the experimental data, with the exception of the very precise ambient temperature data. X J T H O R

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# THERMODYNAMIC PROPERTIES OF NEON\*

R. D. McCarty and R. B. Stewart  
National Bureau of Standards  
Boulder, Colorado

## Introduction

This laboratory has been engaged for the past three years in an investigation of the P-V-T surface of neon including regions where no experimental observations exist. Progress has been reported [ 1, 2 ] periodically during the course of this study. The present work extends the range of the P-V-T data given in these earlier references to the liquid region, and provides consistent thermodynamic properties for the entire range. No further compilations are planned for neon until additional experimental measurements become available.

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\*Results of a study made under contract with the National Aeronautics and Space Administration at the National Bureau of Standards, Boulder, Colorado.

### Selection of P-V-T Data

The P-V-T data selected for this correlation and used for the determination of the equation of state parameters, consist of 198 experimental data points [ 3-9 ] and 182 theoretically derived values [ 1, 10 ]. The experimental data cover a temperature range of 55° to 300°K at pressures from 20 to 200 atm. The theoretical values consist of 143 points for temperatures between 60° and 300°K at pressures from 100 to 200 atm given by McCarty et al. [ 1 ] and 39 values determined from the generalized equation of state given by Hirschfelder et al. [ 10 ] for temperatures from 25° to 45°K at pressures from 100 to 200 atm. Additional theoretical values, particularly for the low pressure liquid were not used in determining the coefficients for the equation of state, but are considered in a later section on P-V-T deviations.

The selection of the liquid neon P-V-T data calculated by Hirschfelder's generalized equation of state, was based on the validity of this equation in applications for other cryogenic liquids which have been studied in this laboratory as well as the satisfactory agreements with experimental data obtained by Hirschfelder et al. in their presentation of this equation. A comparison of the experimental [ 3-9 ] and the theoretical [ 1 ] P-V-T data for neon with values generated by Hirschfelder's generalized equation of state, revealed marked deviations with increasing temperatures, and indicated the best agreement ( $\sim \pm 1\%$  average deviation in density) at the lowest isotherm for both the experimental and the theoretical data. On these bases, it was decided to use data calculated by Hirschfelder's equation of state, but to limit these data to the liquid region.

### Fixed Point Data

The fixed point data for neon used in this correlation are:

Critical Pressure [ 4 ]	26.19 atm
Critical Temperature [ 4 ]	44.40°K
Critical Density [ 5 ]	0.4835 gm/cc
Normal Boiling Temp. [ 4 ]	27.09°K
Density sat. liq. at N. B. P. (equ. 1)	1.206 gm/cc
Density sat. vapor at N. B. P. (equ. 1)	0.009526 gm/cc
Triple point pressure [ 4 ]	0.4273 atm
Triple point temperature [ 4 ]	24.54°K
Density sat. liq. at triple pt. (equ. 1)	1.248 gm/cc
Density sat. vap. at triple pt. (equ. 1)	0.004388 gm/cc
Molecular Weight [ 11 ]	20.183

### The Equation of State

The equation of state selected for this work was developed by Strobridge [ 12 ] for a correlation of thermodynamic properties of nitrogen.

$$\begin{aligned}
 P \text{ (atm)} = & \rho RT + (n_1 T + n_2 + n_3/T + n_4/T^2 + n_5 T^4) \rho^2 \\
 & + (n_6 T + n_7) \rho^3 + n_8 T \rho^4 \\
 & + \rho^3 (n_9/T^2 + n_{10}/T^3 + n_{11}/T^4) e^{-n_{16} \rho^2} \\
 & + \rho^5 (n_{12}/T^2 + n_{13}/T^3 + n_{14}/T^4) e^{-n_{16} \rho^2} \\
 & + n_{15} \rho^6,
 \end{aligned} \tag{1}$$

where  $R = 0.820574 \times 10^{-1}$  and the coefficients in (1) for neon are:

$$\begin{array}{ll}
 n_1 = 0.15560400 \times 10^{-2} & n_9 = 0.53957057 \times 10^2 \\
 n_2 = -0.24655057 & n_{10} = -0.48134170 \times 10^4 \\
 n_3 = 0.43101700 \times 10^1 & n_{11} = 0.95157528 \times 10^5 \\
 n_4 = -0.16879375 \times 10^3 & n_{12} = -0.33474863 \times 10^{-1} \\
 n_5 = 0.26561720 \times 10^5 & n_{13} = -0.96397645 \times 10^1 \\
 n_6 = 0.53180519 \times 10^{-4} & n_{14} = 0.51358579 \times 10^3 \\
 n_7 = 0.45629059 \times 10^{-3} & n_{15} = 0.11034879 \times 10^{-7} \\
 n_8 = -0.67079094 \times 10^{-6} & n_{16} = 0.634 \times 10^{-2}
 \end{array}$$

T is in °K and  $\rho$  is in g-mol/liter. By a method of least squares, the coefficients  $n_1$  through  $n_{15}$  for (1) were obtained by fitting (1) in the form of  $(P/\rho RT - 1) = f(\rho, T)$  to the data outlined above. Coefficient  $n_{16}$  was found by successive approximations. The experimental data were weighted by a factor of five with respect to the rest of the data. The results of the fitted equation are summarized as follows:

Root mean square of the deviations in $(P/\rho RT - 1)$	0.0139
Average percentage deviation in P for the 198 experimental values	$\pm 0.309\%$
Average percentage deviation in P for the 182 theoretical values	$\pm 0.735\%$
Average percentage deviation in $\rho$ for the 198 experimental values	$\pm 0.352\%$
Average percentage deviation in $\rho$ for the 182 theoretical values	$\pm 0.254\%$

The deviation of the P-V-T coordinates as predicted by this equation from observed values is discussed in more detail below.

### Vapor Pressure Equation

The vapor pressure equation given by Grilly [ 4 ] was selected to define the saturation boundary when using (1).

$$\log_{10} P(\text{mmHg}) = 7.46116 - 106.090T^{-1} - 3.56616 \times 10^{-2} T + 4.11092 \times 10^{-4} T^2 \quad (2)$$

The derivative of (2) with respect to temperature at the critical point agrees with the value for neon reported by Riedel [ 13 ].

### P-V-T Deviations

The accuracy of the P-V-T values as predicted by (1) is summarized in Fig. 1.

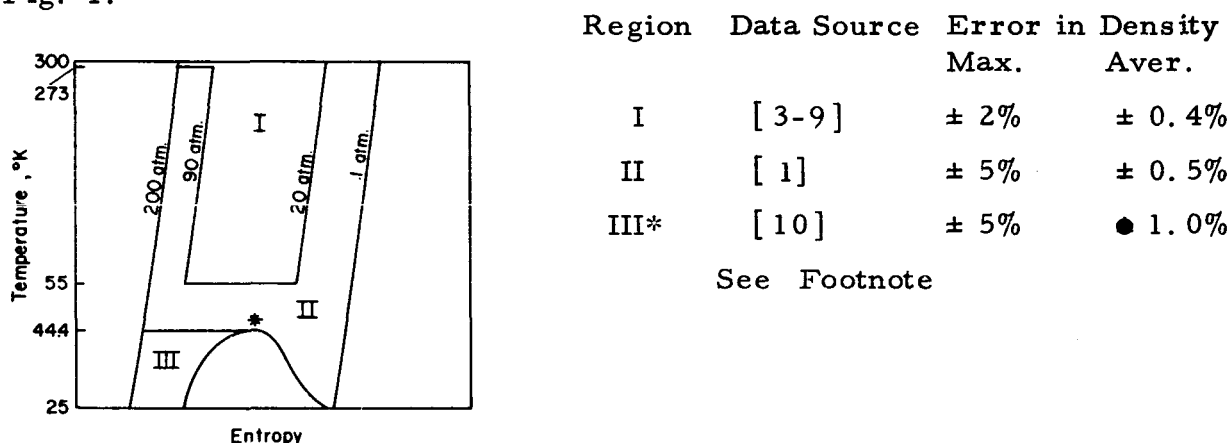


Fig. 1. Estimation of Accuracy and Sources of Data for Various Regions

\* The reader is cautioned in using (1) for calculating pressures for the saturated liquid since large errors result in the pressure although the density approximation is quite good. Very near the critical point, where  $(\partial P / \partial \rho)_T$  is close to zero, the reverse behavior is true, the pressure approximation is good but large errors in density are encountered.

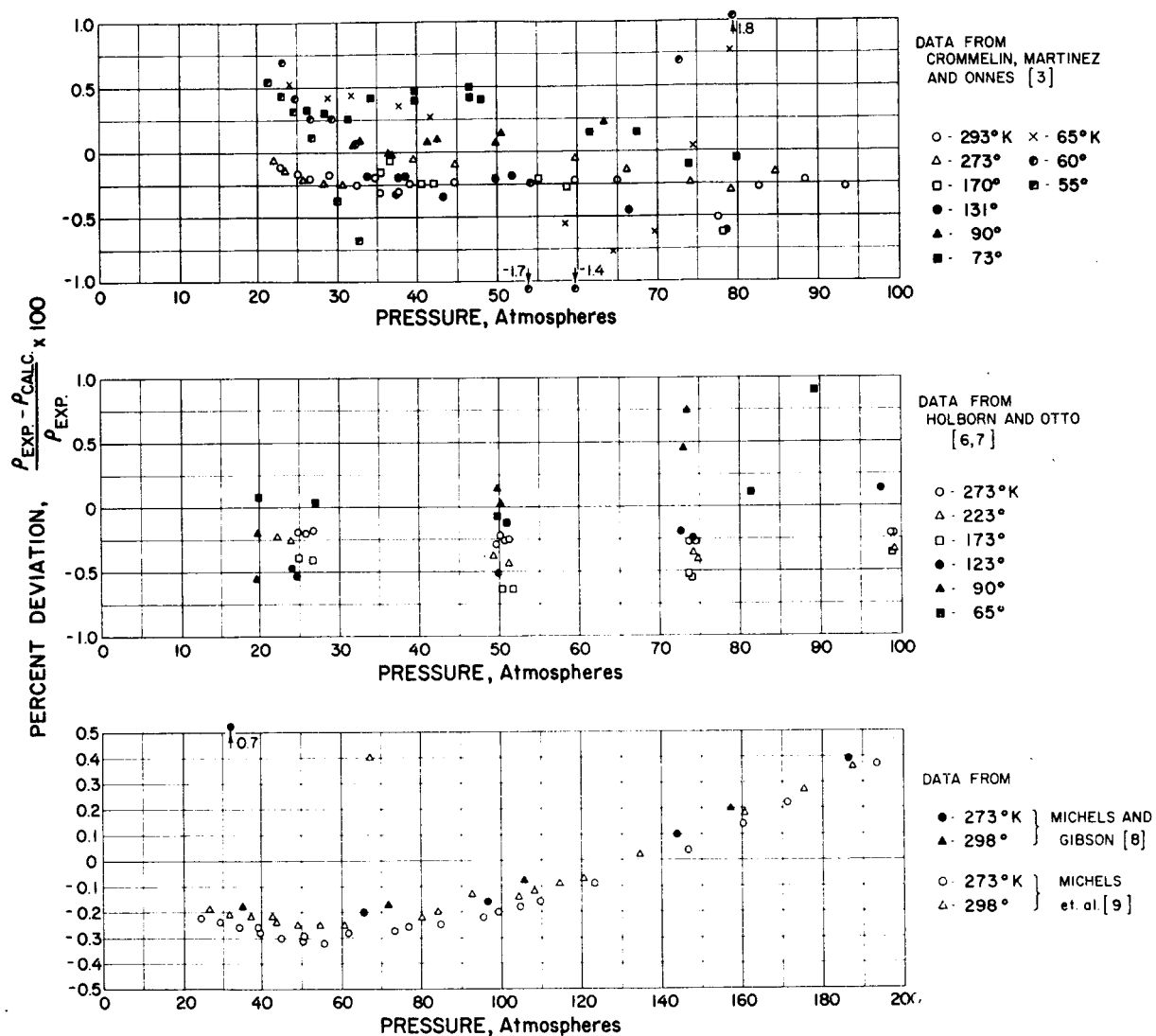


Fig. 2 Deviations of Calculated Densities for Neon from Experimental Points



Estimation of the accuracy of the P-V-T surface predicted by (1) in region I is based on the deviation plots of Fig. 2. (Michels' data above 200 atm are not included in Fig. 2. The maximum deviation in pressure between (1) and Michels' data up to 2000 atm is + 6% at 1300 atm and 0°C; deviations in density were all less than  $\pm 4\%$ .)

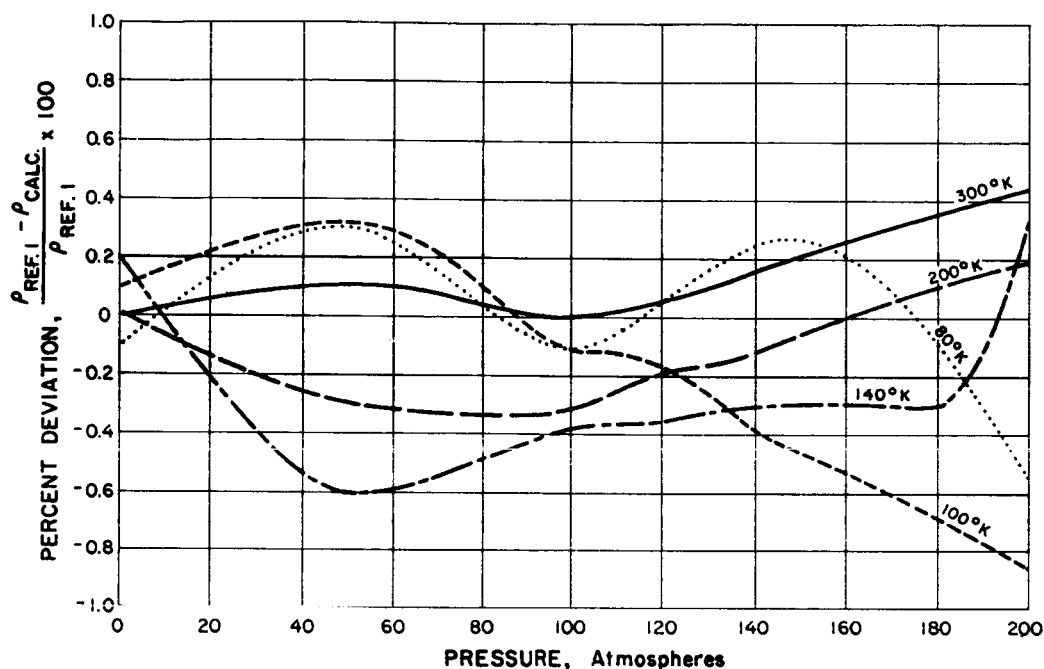


Fig. 3 Deviations of Calculated Densities for Neon

Figure 3 compares the P-V-T values predicted by (1) with values obtained by the authors [1] using corresponding states theory. The maximum variations illustrated in Fig. 3 indicate deviations which are less than the uncertainties ( $\pm 5\%$  in density) in the values given in [1].

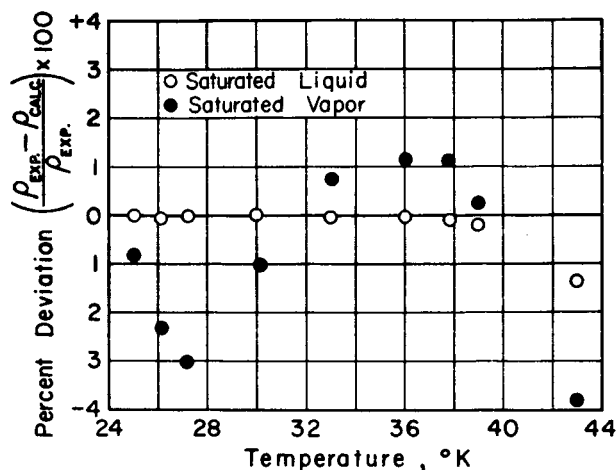


Fig. 4. Deviations between Experimental [ 5 ] and Calculated Saturation Densities for Neon

Efforts to obtain a correspondence between the liquid surfaces of argon and neon using the theory of corresponding states and an argon model were unsuccessful. Therefore no comparison of (1) in region III was possible other than with the generalized equation of state by Hirschfelder. The estimation of accuracy given in Fig. 1 for region III is based solely on the agreement with experimental saturated liquid densities and the physical behavior of other fluids in the liquid region, i. e., the density dependence upon pressure is small.

The reader is reminded that no experimental data are available in regions II and III and that the estimations of accuracy given for these two regions are based on the reliability of the values taken from [ 1 ] and the Hirschfelder equation [ 10 ].

The densities of the saturated liquid and vapor calculated by (1), when the saturation boundary is defined by (2), are compared with the existing experimental points by Crommelin et al. in Fig. 4. It is speculated that the larger deviations in Fig. 4 for the densities of the saturated vapor near the

triple point are, at least in part, due to the inexactness of the data, while the deviations near the critical point are due to the inability of (1) to reproduce the experimental data.

The evaluation of (1) for the critical temperature, 44.40°K and the critical density, 0.4835 gm/cc yields a pressure of 26.85 atm as compared to the critical pressure of 26.19 atm given by Grilly [4].

### Derived Properties

The thermodynamic properties for neon were calculated from the following equations where the absolute value of entropy and internal energy are taken to be zero for the saturated liquid at the triple point.

$$S_{T,\rho} = S_{T_o}^o + \int_{T_o}^T \frac{C_P^o}{T} dT + R \ln (\rho R T) + \int_0^\rho \left[ \frac{R}{\rho} - \frac{1}{\rho^2} \left( \frac{\partial P}{\partial T} \right)_\rho \right] d\rho, \quad (3)$$

where  $S_{T_o}^o$  (3.3987030 j/gm °K) is the reference entropy of the ideal gas at  $T_o$  (27.09°K) and 1 atm.  $C_P^o$  (1.0299 j/gm - °K) is the ideal gas specific heat for neon reported by Rossini [14] which is constant over the range of temperatures considered here.

$$H_{T,\rho} = H_{T_o}^o + \int_{T_o}^T C_P^o dT + (Z-1) RT + \int_0^\rho \left[ \frac{P}{\rho^2} - \frac{T}{\rho^2} \left( \frac{\partial P}{\partial T} \right)_\rho \right] T d\rho \quad (4)$$

where  $H_{T_o}^o$  (92.443001 j/gm) is the reference enthalpy of the ideal gas at  $T_o$ .

$$\Delta S_{\text{vap.}} = \frac{dP}{dT} \Delta V_{\text{vap.}} \quad (5)$$

$$\Delta S_{\text{liq.}} = \int_{\rho_{\text{sat}}}^{\rho} \left[ -\frac{1}{2} \left( \frac{\partial P}{\partial T} \right)_{\rho} \right]_T d\rho. \quad (6)$$

$$\Delta H_{\text{liq.}} = \int_{\rho_{\text{sat}}}^{\rho} \left[ \frac{P}{2\rho} - \frac{T}{2} \left( \frac{\partial P}{\partial T} \right)_{\rho} \right]_T d\rho + \frac{P}{\rho} - \left( \frac{P}{\rho} \right)_{\text{sat.}} \quad (7)$$

$$U = H - PV. \quad (8)$$

The sequence of calculations using the above equations is as follows: the properties of the saturated vapor were calculated first using (3) and (4); the Clapeyron relation (5) was then used to establish the properties for the saturated liquid with values of  $\Delta V_{\text{vap}}$  calculated from solutions of (1) and (2) and  $dP/dT$  from (2). The saturated liquid line as determined was then used as a reference for calculating the entropy and enthalpy for any temperature below critical and densities greater than the saturated liquid using (6) and (7). Calculations for all remaining coordinates of temperature and density were performed using (3) and (4).

A change in  $(\partial S/\partial T)_P$  occurs in the isobars in region III at temperatures approaching 44°K, which required a graphical smoothing to effect a smooth transition to the isobars independently calculated for region II. This resulted in an additive correction for entropy of 0.0099 j/gm - °K at 44°K, for all isobars greater than the critical pressure, and a corresponding additive correction of 0.43 56 j/gm for enthalpy. Inasmuch as these corrections are the same for all isobars they were applied by adding the respective amounts

to  $\Delta S_{\text{vap}}$  and  $\Delta H_{\text{vap}}$  at 44°K.

A comparison of changes in entropy between points of state from these calculations and those reported by Stewart and Johnson [ 2 ] show a mean deviation of 0.56%. The points of state were selected to cover the entire range of pressure and temperature of the Stewart and Johnson data. The larger deviations (1 to 2%) occurred with differences involving points taken at 55°K.

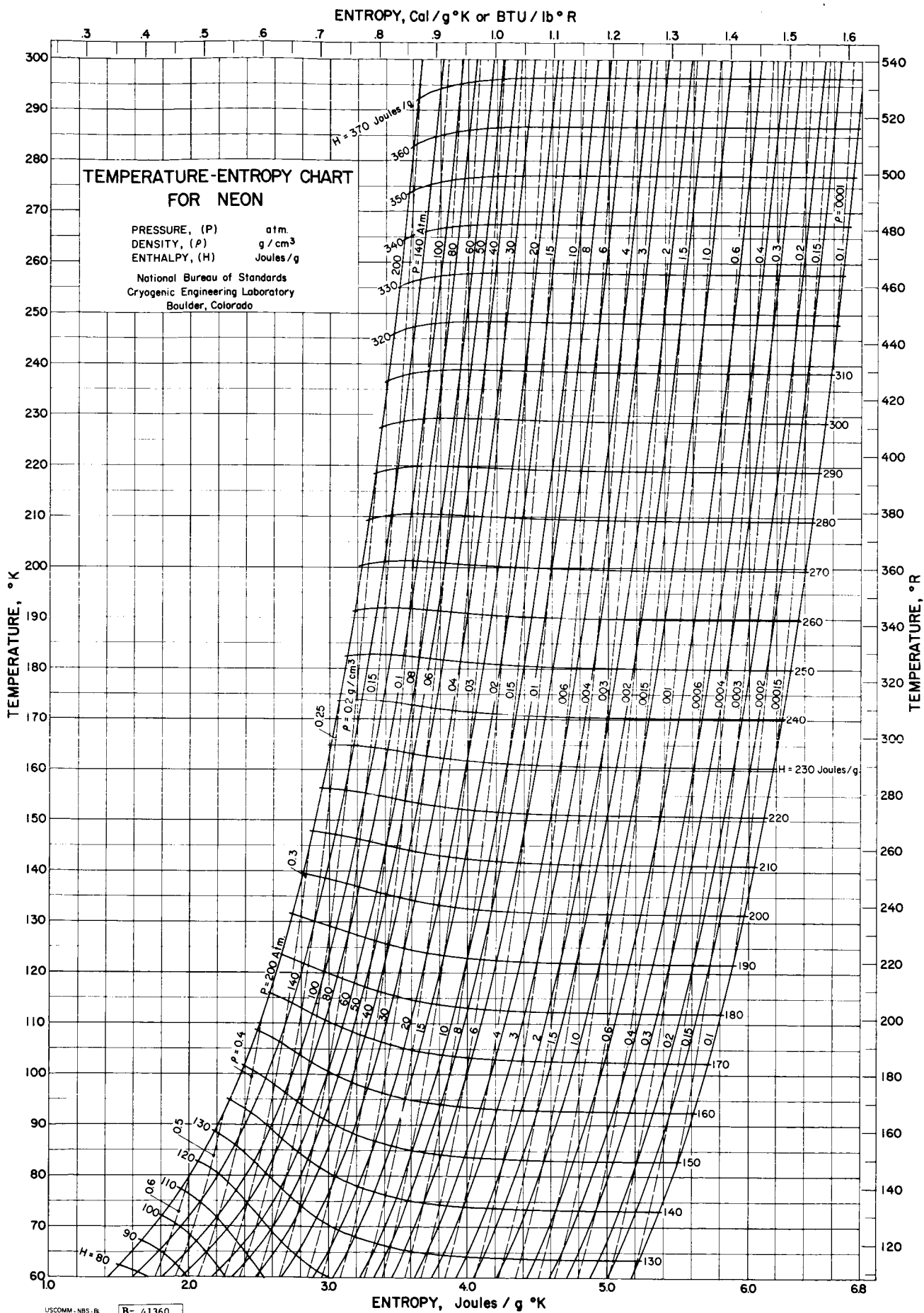
The uncertainties in the derived properties reported herein are necessarily greater than the uncertainties in the P-V-T surface from which they were calculated. In particular, non-typical behavior of the isobars between 100 and 200 atm for temperatures from 50° to 60°K on T-S coordinates has been noted. As there are no existing experimental data for comparisons in this region of pressure and temperature, nothing further may be said.

A large temperature-entropy diagram (dimensions 17 x 22 in.) as well as tabular values will be available in the near future from the Cryogenic Data Center, National Bureau of Standards, Boulder, Colorado.

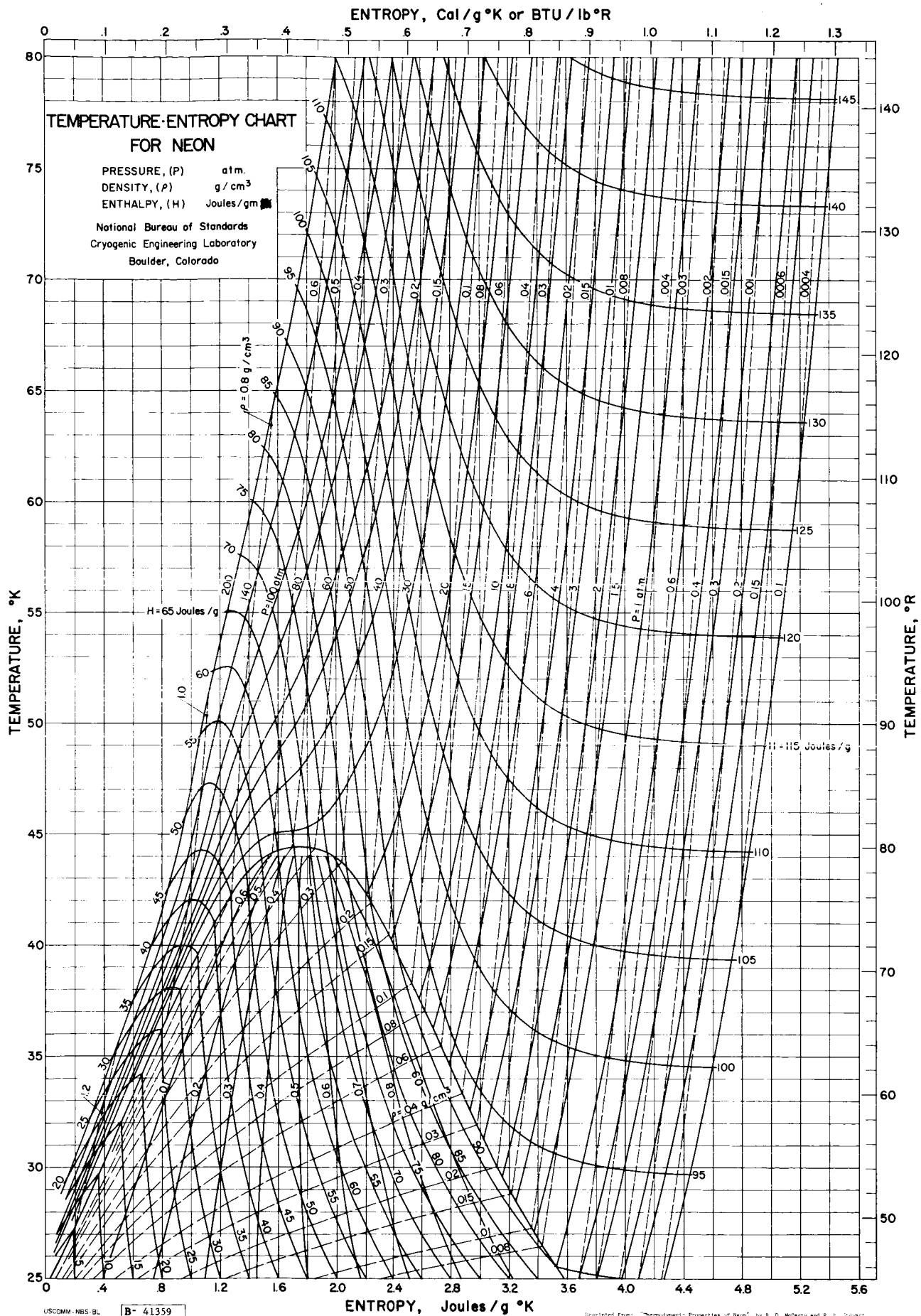
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